Monte Carlo simulations of structural properties and infrared spectra of SF₆-(Ar)ₙ clusters

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A method for predicting the perturbed infrared spectrum of a solvated chromophore such as SF₆ in a mixed van der Waals cluster is developed and applied to a realistic model for SF₆-(AR)ₙ clusters with n = 1-100. The dominant contribution to the band shift arises from the interaction of an induced dipole on the perturber with the oscillating instantaneous dipole of the vibrationally distorted SF₆. Spectra generated by Monte Carlo averaging these frequency shifts over a canonical distribution of cluster configurations and over a plausible assumed cluster size distribution are in near-quantitative agreement with experiment. For the smaller clusters (n ≤ 18), features of the simulations point to the presence of two distinct classes of cluster structure, one in which the chromophore is wrapped in a unimolecular layer of atoms, and a second in which the solvent atoms have multilayered structures. However, the question of whether the infrared spectra can provide evidence for the presence of the kind of phase coexistence identified in simulations for pure Ar clusters is not yet settled.

I. INTRODUCTION

In recent years, considerable attention has been focused on the problem of understanding the structure and dynamics of atomic and molecular clusters.¹ ² ³ ⁴ ⁵ ⁶ ⁷ ⁸ ⁹ ¹⁰ ¹¹ ¹² Notable theoretical work has included a number of Monte Carlo and molecular dynamics simulations of the thermodynamic properties of van der Waals clusters of pure noble gas atoms. One intriguing result of those studies was the prediction that for small clusters there exists a sharply defined region of solid-liquid phase coexistence spanning a narrow temperature range which changes with cluster size. This behavior has been explained by Berry and co-workers within the framework of an analytical theory for rigid-nonrigid transitions, but no unambiguous experimental confirmation of these predictions has yet emerged.

One of the most promising experimental techniques for studying van der Waals clusters is infrared photofragmentation spectroscopy in molecular beams.¹³ In these experiments, a beam of clusters containing an infrared-active chromophore molecule is formed in a nozzle expansion source, and directed across the path of an intense, tunable infrared laser. Absorption of a single photon then (often) leads to vibrational predissociation of the cluster, an event which may be observed either by net depletion of the original beam, or by detection of cluster fragments deflected away from the beam axis.

Some of the earliest experiments of this type used observations of main beam depletion to study the infrared spectra of Ar clusters seeded with a single SF₆ molecule.¹⁴ In this case, the ν₆ band of SF₆ was found to shift monotonically to the red as increases in the nozzle source backing pressure led to increases in the average cluster size. At the same time, the spectral bandwidth was observed to have a local maximum for a relatively narrow range of nozzle pressures. The present work was initiated as an effort to quantitatively explain these results in terms of the nature of the intermolecular forces governing the dynamics of such clusters.

In a preliminary account of the present work,¹⁶ it was suggested that a line broadening observed in the simulated spectra for a relatively narrow range of cluster sizes might be due to phase coexistence. Our subsequent molecular dynamics simulations showed that this is not the case.¹⁷ However, those preliminary molecular dynamics calculations did confirm the existence of a solid-liquid phase transition for these mixed clusters at temperatures near 20 K, and showed that structural symmetry features of medium sized clusters gave rise to the line broadening referred to above. The present paper presents and tests the model on which all of these simulations have been based, and summarizes the results of extensive Monte Carlo calculations for SF₆-(Ar)ₙ systems.

A general theory of frequency shifts was first developed by Buckingham for the case of a dissolved chromophore whose vibrations are perturbed by the surrounding atoms or molecules of a fluid.¹₈ ¹₉ Only recently, however, have advances in our quantitative knowledge of intermolecular potentials made it feasible to apply this type of approach quantitatively to real systems. A review of work on frequency shifts in fluids, with particular attention paid to the question of the pressure dependence, may be found in a recent paper by Zakin and Herschkach.²⁰

A similar perturbation theory of frequency shifts was developed by Friedmann and Kimel for the case of chromophore molecules frozen into noble gas matrices.²¹ More recent work on this problem has focused attention on molecular hydrogen in noble gas crystals²²-²⁴ and on N₂ trapped in nitrogen and rare gas matrices.²⁵ ²⁶ However, despite progress in the experimental techniques of high resolution matrix spectroscopy,²⁷ a full theoretical explanation of frequency shifts in matrix spectra is not yet available.

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The problem of the theoretical description of frequency shifts in clusters, which is addressed in the present work, is closely related to the liquid and matrix cases. As for matrices, few systems have yet been studied quantitatively, the exceptions being the vibrational spectra of clusters of pure SF₆,²⁸ N₂O,²⁹ and H₂O.³⁰ However, prior to the present work,¹⁶,¹⁷ no detailed simulations of the spectra of mixed clusters had been reported.

In the spirit of earlier work,¹⁸⁻²² the vibrational frequency shift of an SF₆ molecule within a cluster is attributed to a sum over perturbations due to the surrounding (Ar) solvent atoms. The present method of predicting these shifts is described in Sec. II, where it is shown that the dominant contribution to the perturbing potential arises from the interaction of the instantaneous oscillating dipole field of the molecule with the dipole it induces in the surrounding Ar atoms. A simplified approximate continuum model for large clusters is also presented there, as is a description of the Monte Carlo method used for averaging the predicted shifts over the thermally accessible cluster structures. The results of the simulations are presented and compared with experiment in Sec. III, while Sec. IV summarizes our conclusions.

II. SIMULATING THE CLUSTER SPECTRA

A. Perturbation of the SF₆

In the harmonic model used here, the anharmonicity and rotational degrees of freedom of the SF₆ are neglected, as they are expected to have little effect on the properties of interest. As the various vibrational motions are therefore orthogonal, the SF₆ molecule may be treated simply as a three-dimensional harmonic oscillator with the atoms moving according to the triply degenerate ν₁ mode.¹¹ The definition of the molecule's body-fixed coordinate system and the nature of the atom's displacements associated with this mode²⁻³⁴ are shown in Fig. 1. In the present discussion, the center of mass of the SF₆ molecule is placed at the coordinate system origin, and the S–F bonds are aligned along the X, Y, and Z axes.

The eigenstates of SF₆ relevant here are the ground state |0⟩ and the three degenerate first excited ν₁ states |1₁⟩, where i = 1–3 correspond to motion in the X, Y, and Z directions, respectively. The influence of the surrounding cluster atoms on these oscillator levels is governed by the total perturbing potential \(V_p(\{\mathbf{R}_i\}, \{\mathbf{Q}_i\})\), which in turn depends on the positions \(\mathbf{R}_i\) (j = 1, 2, ..., n) of the n Ar atoms in the cluster and the normal coordinates \(Q_i\) (i = 1–3) which characterize the displacements of the atoms within the SF₆ molecule. Neglecting three-body and higher-order interactions, the perturbing potential may be written as a sum over the individual Ar–SF₆ pair potentials \(V_p(\{\mathbf{R}_i\}, \{\mathbf{Q}_i\})\):

\[
V_p(\{\mathbf{R}_i\}, \{\mathbf{Q}_i\}) \equiv \sum_{i=1}^{\infty} V(\mathbf{R}_i, \{\mathbf{Q}_i\}).
\]

Since the intramolecular displacements represented by the \(\{\mathbf{Q}_i\}\) are small compared to the S–F bond lengths,⁴² \(V(\mathbf{R}_i, \{\mathbf{Q}_i\})\) may be expanded in powers of these displacement coordinates:

\[
\begin{align*}
V(\mathbf{R}_i, \{\mathbf{Q}_i\}) &= V_0(\mathbf{R}_i) + \sum_{i=1}^{3} \frac{\partial V}{\partial Q_i} Q_i \\
&+ \frac{1}{2} \sum_{i=1}^{3} \sum_{k=1}^{3} \frac{\partial^2 V}{\partial Q_i \partial Q_k} Q_i Q_k + \cdots,
\end{align*}
\]

where \(V_0(\mathbf{R}_i)\) is the atom plus rigid molecule Ar–SF₆ potential for \(\{\mathbf{Q}_i = 0\}\).

In first-order perturbation theory, the shift of the ground state energy level |0⟩ is given simply by

\[
\Delta E_0 = \langle 0 | V_p | 0 \rangle,
\]

while for the triply degenerate first excited states |1₁⟩, the level shifts \(\Delta E_{1₁}(i = 1–3)\) are the roots of the secular equation

\[
\text{det}[\langle 1_i | V_p | 1_k \rangle - \Delta E_{1₁} \delta_{i,k}] = 0.
\]

As is schematically illustrated by Fig. 2, the frequency shifts in the infrared spectrum then arise from the differences between the level shifts of the |1₁⟩ and |0⟩ states,

\[
\Delta \nu_{1₁} = (\Delta E_{1₁} - \Delta E_0)/\hbar c.
\]

If the cluster has the same symmetry (O₃h) as the SF₆ molecule, the three \(\Delta E_{1₁}\) values will be equal. In general, however, the cluster has lower symmetry, so the degeneracy of the \(\Delta E_{1₁}\) is removed and the spectral line is split into two or three components.

The first term on the right-hand side of Eq. (2) does not depend on the normal coordinates \(\{\mathbf{Q}_i\}\). Its contributions to \(\Delta E_0\) and \(\Delta E_{1₁}\) are therefore the same, and it has no effect on the \(\Delta \nu_{1₁}\). The terms linear in \(\mathbf{Q}_i\) also make no contribution to the frequency shifts, because they depend on matrix elements of the form \(\langle 0 | Q_i | 0 \rangle\) and \(\langle 1_i | Q_i | 1_k \rangle\) which are identically zero for any symmetric oscillator. For similar reasons, first-order contributions associated with all higher odd powers of (products of) the \(\mathbf{Q}_i\) are also zero. It is therefore the
\[ \langle 1 | V' | 1_k \rangle = \sum_{j=1}^{n} \left[ V_0(R_j) \delta_{jk} + \frac{\hbar}{4\omega} \right] \times \left( 2 \frac{\partial^2 V}{\partial Q_j \partial Q_k} + \delta_{jk} \sum_{r=1}^{m} \frac{\partial^2 V}{\partial Q_r^2} \right). \] (8)

Thus, once the potential derivatives of Eq. (2) are known, the frequency shifts of Eq. (5) may be readily generated from Eqs. (7) and (8) and the roots of the $3 \times 3$ secular determinant of Eq. (4).

**B. The Ar-SF$_6$ interaction potential**

In order to calculate frequency shifts using the perturbation scheme described above, the Ar-SF$_6$ pair potential $V(R_j, \{Q\})$ must be known. An excellent approximation to the strongly anisotropic atom plus rigid-molecule portion of this potential, $V_0(R_j)$, has been determined by Pack et al.\textsuperscript{37} from a simultaneous fit to total differential scattering cross sections, viscosities, and virial coefficient data. Its radial behavior along the three characteristic symmetry axes of SF$_6$ is shown in Fig. 3. This potential, together with the Ar-Ar pair potential,\textsuperscript{38} determines the structure of the SF$_6$-\(\text{Ar}_n\) clusters.

As mentioned above, there is little independent information regarding the dependence of the Ar-SF$_6$ pair potential on the SF$_6$ stretching coordinates $\{Q\}$, and there is no unique way of adding such stretching dependence to the atom plus rigid-molecule potential of Pack et al.\textsuperscript{37} The most straightforward approach to the latter problem would be to represent the Ar-SF$_6$ potential as a sum of Ar-S and Ar-F pair potentials, $u_{\text{Ar-S}}$ and $u_{\text{Ar-F}}$:

\[ V(R_j, \{Q\}) = u_{\text{Ar-S}} [R_j - r_s(\{Q\})] \]
\[ + \sum_{j=1}^{6} u_{\text{Ar-F}} [R_j - r_{F_l}(\{Q\})], \] (9)

where $r_s$ denotes the position of the S atom and $r_{F_l}$ ($l = 1, 2, \ldots, 6$) the positions of the six F atoms. If effective atom-

![FIG. 3. Radial behavior of the empirical Ar-SF$_6$ potential energy surface of Pack et al. (Ref. 37) along the two, three, and fourfold molecular symmetry axes of SF$_6$.](image-url)
atom pair potentials \( u_{\text{Ar-S}} \) and \( u_{\text{Ar-F}} \) are determined, subject to the requirement that they provide a "good" representation of the known \( \{ \mathcal{Q}_m = 0 \} \) potential \( V_0(\mathbf{R}_t) \), stretching dependence is automatically introduced by the fact that \( r_t \) and \( r_{t_k} \) are known functions of the intramolecular displacement coordinates \( \{ \mathcal{Q}_m \} \). However, this approach has two shortcomings. The first is that this atom–atom potential sum cannot take proper account of the inherently nonlocal instantaneous dipole–induced dipole contribution to the interaction (which is shown below to provide the dominant contribution to the level shifts). The second is simply the fact that it may be difficult to devise a pairwise additive potential of the form of Eq. (9) which provides an accurate representation of \( V_0(\mathbf{R}_t) \); this latter question is examined next.

Billing\(^{30}\) fitted a potential of the form of Eq. (9) to the rigid-molecule potential \( V_0(\mathbf{R}_t) \) of Ref. 37 while representing the component Ar–S and Ar–F pair potentials as simple double exponential functions:

\[
 u(r) = A e^{-ar} - B e^{-br}, \tag{10}
\]

As in the present work, his potential parameters were determined by optimizing agreement with radial behavior of the Pack et al.\(^{37}\) potential along the three characteristic symmetry axes. Figure 4 shows the relatively poor agreement between his function (dashed curves) and the Pack et al.\(^{37}\) potential (solid curves). In attempting to improve on this agreement, we first considered the more realistic Tang–Toennes form\(^{40}\) for the atom–atom potentials:

\[
 u(r) = A e^{-br} - \sum_{n=0}^{\infty} \left[ 1 - e^{-br} \sum_{k=0}^{2n} \frac{(br)^k}{k!} \right] \frac{C_{2n}}{r^{2n}}, \tag{11}
\]

However, use of this more flexible radial function yielded no better agreement than was achieved by Billing.\(^{30}\) More generally, in all fits to the Pack et al.\(^{37}\) potential which treated \( u_{\text{Ar-S}} \) and \( u_{\text{Ar-F}} \) in Eq. (9) as simple radial functions, the curve for the behavior of the potential along the twofold symmetry axis (the middle curve in Figs. 3 and 4) lay much closer to the potential for the threefold axis than to that for the fourfold axis. In contrast, for the surface of Pack et al.\(^{37}\) (solid curves), the potential along this twofold axis lies approximately midway between the other two.

Much better agreement with this behavior was achieved by introducing an anisotropic Ar–F potential with axial symmetry around the S–F bonds,

\[
 u_{\text{Ar-F}}(r_t, \theta_t) = A \left[ 1 + p P_2(\cos \theta_t) \right] e^{-br_t} - \sum_{n=2}^{\infty} \sum_{k=0}^{2n} \left( \frac{(br_t)^k}{k!} \right) \frac{C_{2n}}{r_t^{2n}}, \tag{12}
\]

where \( r_t = |\mathbf{R}_t - \mathbf{r}_{p_t}| \), \( \theta_t \) is the angle subtended by \( (\mathbf{R}_t - \mathbf{r}_{p_t}) \) and \( (\mathbf{r}_t - \mathbf{r}_{p_t}) \), and \( P_2(\cos \theta_t) = [3 \cos^2(\theta_t) - 1] / 2 \). The series of dispersion terms was truncated after \( 2n = 10 \), since higher power terms have little effect, while the constraint

\[
 C_{2n}(\text{Ar–S}) + 6C_{2n}(\text{Ar–F}) = C_{2n}(\text{Ar–SF}_6) \tag{13}
\]

was applied to the coefficients for \( n = 3–5 \), where \( C_{2n}(\text{Ar–SF}_6) \) are the dispersion constants of Pack et al.\(^{37}\) This fit yielded the parameter values listed in Table I and the dot–dash curves seen in Fig. 4. The agreement between our surface and the Pack et al.\(^{37}\) potential is clearly very good along the three symmetry axes. However, Fig. 5 shows that there remain distinct differences between the angular behavior of these two functions, especially near the fourfold symmetry axis (\( \theta = 0 \) and \( \pi \)). On the other hand, the present atom–atom potential form might still provide a good fit to the experimental data on which the Pack et al.\(^{37}\) surface was based.

In any case, it is clear that obtaining an accurate representation of the Pack et al.\(^{37}\) Ar–SF\(_6\) potential using the pairwise additive ansatz of Eq. (9) is not a simple matter. Better agreement than that seen in Fig. 5 could certainly be attained by introducing more sophisticated \( \theta_t \)-dependent behavior, and/or adding terms such as an interaction between the atom and the midpoints of the S–F bonds. However, this question was not pursued further, for as is shown below, the stretching dependence introduced through Eq. (9) provides

\[
\begin{array}{c|c|c}
\text{Ar–S} & \text{Ar–F} \\
\hline
A (eV) & 0^a & 15.7 \\
F & 0^b & -0.675 \\
b (\text{Å}^{-2}) & 4.00^b & 4.23 \\
C_6 (eV \text{Å}^6) & 117 & 5.52 \\
C_8 (eV \text{Å}^8) & 1021 & 0^a \\
C_{10} (eV \text{Å}^{10}) & 8437 & 0^a \\
\end{array}
\]


\( ^a \) Parameter fixed at zero because interparameter correlation prevented the fit to the Pack et al.\(^{37}\) potential from determining an independent value for it.

\( ^b \) Value set arbitrarily; only relevant for damping of the dispersion terms.

![FIG. 4. Comparisons of the radial behavior of the Pack et al. (Ref. 37) potential along the three characteristic symmetry axes (solid curves, as in Fig. 3), with those of the approximate surface Billing (Ref. 39) generated using Eqs. (9) and (10) (dashed curves), and with the present potential of Eqs. (9) and (12) and Table I (dot–dash curves).](image-url)
only a minor contribution to the frequency shifts and splittings. Hence, in the simulations described herein, the Ar-SF$_5$ pair potential was represented simply by the rigid-molecule $V_0(R)$ potential of Pack et al.,$^{37}$ while the (nonlocal) stretching dependence which gives rise to the frequency shifts was introduced through the model described below.

C. The instantaneous dipole–induced dipole mechanism

Because of its symmetry, an SF$_5$ molecule in its equilibrium configuration $\{Q_i = 0\}$ has no dipole moment. Moreover, for vibrational motion governed by a symmetric potential, such as that for the $v_3$ mode of SF$_5^{19}$, the average value of the dipole moment is zero independent of whether or not the motion is harmonic. As a result, the SF$_5$ molecule vibrating in the $v_3$ mode(s) has no permanent dipole moment, independent of the degree of excitation. However, when displaced from equilibrium in the course of the $v_3$ vibrational motion, an instantaneous electric dipole moment arises. For small displacements, it may be approximated as a linear function of the displacement coordinates $\{Q_i\}$: $$\mu = \sum_{i,j=1}^{3} \frac{\partial \mu}{\partial Q_i} Q_j e_i,$$ (14)

where the $\{e_i\}$ are unit vectors in the $X$, $Y$, and $Z$ directions. The coefficient $\partial \mu / \partial Q_3$ appearing here can be deduced from the measured intensity of the $v_3$ band of an isolated SF$_5$ molecule, and the value reported in the literature is 226 esu $\cdot$ cm$^{-1}$.$^{41}$ This corresponds to a transition dipole moment of $^{42}$ $\langle 1 | \mu | 0 \rangle = 9/2\omega (\partial \mu / \partial Q_3) = 0.388$ D, where $\omega = 2\pi c = 948$ cm$^{-1}$, and 1 D = $10^{-18}$ esu cm.

The instantaneous dipole $\mu$ appearing on an SF$_5$ molecule in the course of its vibration gives rise to an electric field $E(R, t)$: $$E(R, t) = \left[ \frac{3 (\mathbf{R}, \mathbf{R}) - \mathbf{R}_J \mathbf{R}_J}{\mathbf{R}_J^5} \right] / \mathbf{R}_J^5$$ (15)
at the positions $\{R_j\}$ of the Ar atoms in the cluster. Ignoring the variation of the electric field $E$ over the atomic volume, the dipole moment induced on the atom is simply $\alpha E$, where $\alpha = 1.642$ A$^3$ is the dipole polarizability of Ar.$^{43}$ The interaction between this induced dipole and the instantaneous dipole on the SF$_5$ molecule then gives rise to the interaction energy

$$V_{id}^{id}(\mathbf{R}, \mu) = -\alpha E(\mathbf{R}, \mu)^2 / 2$$ (16)

which is implicitly part of the atom–molecule potential of Eq. (2), and whose stretching dependence is associated with that of the instantaneous dipole $\mu$ [see Eq. (14)].

Manipulation of Eqs. (14)–(16) yields expressions for the potential derivatives appearing in the energy shifts expressions of Eqs. (4)–(8):

$$\frac{\partial^2 V_{id}}{\partial Q_j \partial Q_k} = -\frac{\partial \mu}{\partial Q_j} \frac{\partial \mu}{\partial Q_k} \left[ \frac{3 R_{ik} R_{jk}}{R_j^2} + \delta_{ik} \right],$$ (17)

where $R_{ik} = R_i - e_i$ denotes the $i$th Cartesian component of the vector $\mathbf{R}_i$ in the molecule fixed coordinate system of Fig. 1. Note that because of the quadratic dependence of $V^{id}$ on $E$ and the linear dependence of $E$ on $\mu$, and hence on the $Q_j$'s, the third and higher derivatives of $V^{id}$ with respect to the $Q_j$ are identically zero, so $V^{id}$ makes no contribution to the higher-order terms omitted from Eq. (2). On replacing $V$ in the derivatives in Eqs. (7) and (8) by $V^{id}$, one obtains

$$\Delta E^{id}_{ij} = \sum_{j=1}^{3} \left[ V_0(\mathbf{R}_j) - \frac{3 \alpha \hbar}{2 \omega R_j^5} \left( \frac{\partial \mu}{\partial Q_3} \right)^2 \right]$$ (18)

and

$$\langle 1_i | \mathbf{V}_p | 1_k \rangle^{id} = \sum_{j=1}^{3} \left[ V_0(\mathbf{R}_j) \delta_{ik} - \frac{\alpha \hbar}{2 \omega R_j^5} \times \left( \frac{\partial \mu}{\partial Q_3} \right)^2 \left( \frac{3 R_{ik} R_{jk}}{R_j^2} + 4 \delta_{ik} \right) \right].$$ (19)

Utilizing these expressions in Eqs. (4) and (5) then yields the frequency shifts due to the induced dipole mechanism for any given cluster structure defined by the set of Ar atom positions $\{R_j\}$.

Examination of the secular determinant obtained on substituting Eq. (19) into Eq. (4) shows that the three eigenvalues $\Delta E_{ij}$ ($i = 1–3$) do not depend on the orientation of the SF$_5$ molecule. Rather, they depend only on the relative positions of the Ar atom(s) and their distance from the chromophore center of mass. This result can be verified formally by applying an arbitrary rotational transformation to the Ar atom coordinates. Such a coordinate transformation leads to an orthogonal transformation of the perturbation matrix, leaving the eigenvalues unchanged. Note that this is true only because for the induced dipole model, the components of $\mathbf{R}_i$ appear in Eq. (19) as the products $R_{ik} R_{jk}$. In other cases, the three eigenvalues will in general depend upon the orientation of the molecule within the cluster.

D. Frequency shift of the Ar–SF$_5$ dimer

This section describes the effect of applying the instantaneous dipole–induced dipole mechanism presented above to
the case of a single Ar atom interacting with an SF₆ molecule. For the vibrationally excited level \( v_3 = 1 \), the three eigenvalues of the secular determinant of Eq. (4) implied by the matrix elements of Eq. (19) are

\[
\Delta E_{1,2}^d = V_0(R) - \frac{\alpha \hbar \lambda_4}{2 \omega R^6} \left( \frac{\partial \mu}{\partial Q_3} \right)^2,
\]

(20)

where \( \lambda_1 = \lambda_2 = 4 \) and \( \lambda_3 = 7 \). The degenerate eigenvalues \( \Delta E_{1,2} \) correspond to SF₆ vibrational motion perpendicular to \( R \), and the third (lower) eigenvalue \( \Delta E_{1,3} \) to motion parallel to \( R \). On substituting Eqs. (18) and (20) into Eq. (5), the resulting expressions for the frequency shifts of SF₆ interacting with a single Ar atom are

\[
\Delta v_{1,2}^d = -\frac{\alpha}{4\pi \omega R^6} \left( \frac{\partial \mu}{\partial Q_3} \right)^2 = -\Delta C_v/R^6
\]

and

\[
\Delta v_3^d = 4\Delta v_{1,2}^d = -4\Delta C_v/R^6.
\]

(22)

Literature values of the quantities \( \omega, \alpha \), and \( \partial \mu/\partial Q_3 \) determine the coefficient \( \Delta C_v = 1247 \text{ cm}^{-1} \text{ Å}^6 \), which is the induced-dipole contributions to the difference between the dispersion energies for an Ar atom interacting with SF₆ in \( v_1 = 0 \) and \( v_1 = 1 \). The predicted frequency shifts obtained from Eqs. (21) and (22) for \( R = 4.2 \text{ Å}, \) the minimum of \( V_0(R) \), are listed in the first row of Table II; the quantity \( \Delta \nu \) shown there is simply the spherical average \( (\Delta v_1 + \Delta v_2 + \Delta v_3)/3 \).

Equations (21) and (22) yield the following important predictions. The perturbing influence of a single Ar atom splits the triply degenerate \( v_3 \) line of the free SF₆ molecule into two components, one of which is doubly degenerate. Both components are shifted to the red [see the minus sign in Eq. (21)], the nondegenerate line being shifted twice as far as the doubly degenerate line. These shifts depend only on the magnitude of \( R \), and not on its direction; i.e., unlike the interaction potential, the shifts are indifferent to the anisotropy of the SF₆ molecule. This is a consequence of the assumption that the SF₆ behaves as an isotropic three-dimensional harmonic oscillator. The prediction that the shifts will be proportional to the inverse sixth power of the radial Ar–SF₆ distance suggests that they should be quite sensitive to the structural arrangements of their nearer neighbors in the cluster.

In Fig. 6, plots of \( \Delta v_{1,2}^d \) and \( \Delta v_3^d \) as function of \( R \) (solid curves, left ordinate scale) are compared with the shifts obtained on also taking into account the stretching dependence of the rest of the interaction potential (dashed curves), the latter being estimated using the atom–atom potential of Table I. The second derivatives of this overall potential (of Table I) with respect to the normal coordinates \( \{Q_i\} \) as required by Eqs. (7) and (8) were evaluated numerically, following application of the usual transformation between the normal and displacement coordinates. While the solid curves in Fig. 6 do not depend upon the SF₆ orientation, the dashed curves do; the latter were calculated for radial motion along the threefold symmetry direction \( X = Y = Z \) where the potential minimum lies. For reference, the dotted curve (right ordinate scale) shows the radial potential along this axis. The shifts yield solely by the atom–atom potential of Table I for an Ar atom at \( R = 4.2 \text{ Å}, \) on this axis are listed in the second row of Table II.

The results in Fig. 6 and Table II clearly show that the instantaneous dipole–induced dipole mechanism yields the dominant contribution to the frequency shifts, and that contributions due to the additive potential ansatz of Eq. (9) are relatively small. Since the stretching dependence of the overall potential is not well known (see Sec. II 2 B), only the instantaneous dipole–induced dipole mechanism is used in the shift calculations reported below. Note, however, that this dominance of the induced dipole mechanism reflects the facts that both the dipole moment derivative \( \partial \mu/\partial Q_3 \) and the atomic polarizability are fairly large for this case, criteria which will not necessarily be satisfied for other systems.

<table>
<thead>
<tr>
<th>( \Delta v_{1,2} )</th>
<th>( \Delta v_3 )</th>
<th>( \Delta \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instantaneous dipole–induced dipole model only</td>
<td>-0.227</td>
<td>-0.908</td>
</tr>
<tr>
<td>Atom–atom potential model of Table I</td>
<td>+0.040</td>
<td>-0.31</td>
</tr>
</tbody>
</table>

E. Continuum model for frequency shifts in large clusters

For clusters containing 100 or more Ar atoms, Monte Carlo or molecular dynamics simulations are not readily feasible, both because they do not converge rapidly, and because of the rapid growth in computational expense with increasing cluster size. The present section describes a simple continuum model for estimating the frequency shifts in such systems. In this model, the frequency shifts are again calculated using the instantaneous dipole–induced dipole mechanism, but the SF$_6$ chromophore is now treated as a sphere of radius $a_c$ and the perturbers as a homogeneous semi-infinite medium with a flat surface and a number density of $\eta$. For the Ar clusters we use $\eta = 4/(a_{foe}^3)$, where $a_{foe} = 5.32$ Å is the face-centered-cubic crystal lattice parameter for solid Ar.

The continuum model is schematically illustrated in the upper portion of Fig. 7 for cases in which the chromophore: (a) is completely outside the perturbing medium, (b) intersects the surface of the medium, and (c) is completely buried in the medium. On replacing the sums over $j$ in Eqs. (18) and (19) by integration over the semi-infinite medium, one obtains simple analytic expressions for the shift(s) of the vibra-

\[ \Delta \nu_1 = \Delta \nu_2 = -\pi \eta \Delta C_6/4a_c^3, \]
\[ \Delta \nu_3 = -\pi \eta \Delta C_6/2a_c^3, \]

for $z > a_c$; 

\[ \Delta \nu_1 = \Delta \nu_2 = -\left[ 16 - 15(z/a_c) + 2(z/a_c)^3 \right] \pi \eta \Delta C_6/12a_c^3, \]
\[ \Delta \nu_3 = -\left[ 16 - 6(z/a_c) - 4(z/a_c)^3 \right] \pi \eta \Delta C_6/12a_c^3, \]

for $a_c > z > -a_c$;

\[ \Delta \nu_1 = \Delta \nu_2 = -\left[ 32 - 3(z/a_c)^3 \right] \pi \eta \Delta C_6/12a_c^3, \]
\[ \Delta \nu_3 = -\left[ 32 - 6(z/a_c)^3 \right] \pi \eta \Delta C_6/12a_c^3, \]

for $-a_c > z$.

where $\Delta C_6 = 1247$ cm$^{-1}$ Å$^6$ is defined as in Eq. (21).

Choosing the effective SF$_6$ radius to be $a_c = 3$ Å yields approximate agreement with the experimental shift of $\sim -10$ cm$^{-1}$ found for the “matrix peak” in large clusters. Combined with a realistic hard sphere Ar radius of 1.6 Å, this yields an Ar–SF$_6$ spacing consistent with the Pack et al. potential (see Fig. 3). The predicted frequency shifts obtained in this way are shown in the lower portion of Fig. 7.

Clearly, replacing the “point perturber” of Eqs. (21) and (22) with a semi-infinite continuum reduces the ratio of the shifts for the parallel and perpendicular bands from 4:1 to an upper limit of 2:1. Moreover, while a splitting persists for most configurations, it disappears both when the chromophore is exactly half buried in the surface, and when it is infinitely far below the surface of the perturbing medium. While this model is not quantitatively appropriate for the cluster sizes of interest here, it proved useful in suggesting a structural explanation for certain features of the simulated spectra.

F. The Monte Carlo averaging procedure

Using the model of Sec. II C, one can readily calculate the frequency shifts of the $\nu_j$ band of SF$_6$ for any given SF$_6$–(Ar)$_n$ cluster structure. However, the number of energetically allowed cluster configurations is quite large at most temperatures, and grows very rapidly with $n$, so a Monte Carlo procedure was used for averaging over the contributions from the thermally accessible structures.

Our calculations typically started from an initial cluster configuration in which the $n$ Ar atoms were randomly distributed on the surface of a sphere of radius 6 Å (or 8 Å for $n > 50$) centered on the SF$_6$ molecule. Following the standard Monte Carlo procedure, the configuration space of the cluster was explored by a series of small random moves chosen so as to sample the canonical distribution of configurations associated with a given temperature $T$. In the present work, this was done using the force bias Monte Carlo method introduced by Pangali, Rao, and Berne as an extension of the basic Metropolis et al. approach.

In each step of the standard method, one randomly selected atom is moved according to the vector $(\delta X, \delta Y, \delta Z)$, where the increments $\delta X, \delta Y,$ and $\delta Z$ are randomly

---

**FIG. 7.** Upper: schematic illustration of the model of a spherical chromophore of radius $a_c$ interacting with a semi-infinite perturbing continuum. Lower: dependence on the chromophore-medium separation $z$ of frequency shifts for the parallel (dashed curve) and perpendicular (solid curve) components of the $\nu_1$ band, as predicted for the perturbing continuum model by Eqs. (23)–(25).
chosen with uniform probability, subject to the constraint that

$$\Delta \leq \langle \delta X, \delta Y, \delta Z \rangle \Delta.$$

This attempted move is then either accepted or rejected according to an acceptance probability which depends on both $T$ and the change in potential energy during this move. In the force bias method, a possible move is selected in the same manner, but the probability of it being accepted is enhanced in the direction of the force acting on that atom. This approach has been shown to speed up convergence to the desired canonical distribution. In our calculations, the parameter which determines the strength of the force bias effect was set equal to 0.5, the standard value used in the literature. The maximum step size selected, $\Delta = 0.4$ Å, then yielded acceptance probabilities ranging from 50% (for $n = 100$) to 80% (for $n = 1$) at $T = 50$ K, and from 35% (for $n = 18$) to 49% (for $n = 1$) when $T = 30$ K.

Following the commencement of each simulation run, results associated with the first $2 \times 10^4$ accepted Monte Carlo moves were discarded in order to minimize sensitivity to the initial configuration. Properties of cluster configurations associated with the remaining moves were then collected and analyzed statistically. In most cases $1 \times 10^6$ accepted moves were deemed sufficient, although some simulations were allowed to run for $3 \times 10^6$ accepted moves in order to reduce the statistical errors. The simulated frequency spectrum was then obtained from the distribution of induced dipole model frequency shifts for this ensemble of cluster structures. This approach clearly assumes that the absorption intensity is independent of cluster structure; while this will not be exactly true, it is a reasonable first approximation, and is used throughout the present work.

At each step of the force bias Monte Carlo calculation, both the total potential energy and the vector force on the Ar atom being moved, must be calculated. In the present work, the potential energy of the cluster was evaluated as a sum over all possible Ar–SF$_6$ and Ar–Ar pair interactions, with three-body and higher-order forces being neglected. In these calculations, the Ar–SF$_6$ potential was represented by the empirical anisotropic (but rigid-body) potential of Pack et al., the function referred to as $V_0(R)$ in Sec. II B.

Extremely accurate Ar–Ar pair potentials have been reported in the literature. However, they usually have analytic forms such as that of Eq. (11), which makes them fairly expensive to use for calculating the $(n - 1)$ Ar–Ar pair interactions which change in every step of the Monte Carlo procedure. For the sake of computational efficiency, we therefore approximated this interaction energy with the simple form

$$V(r) = A_{12}/r^{12} + A_6/r^6 + A_9/r^9,$$

where the parameters $A_6$, $A_9$, and $A_{12}$ were determined from a least squares fit of Eq. (27) to the well region of the Ar–Ar potential recommended by Aziz and Slaman. The resulting potential parameters are listed in Table III. While this potential is not ideal, its inadequacies are much smaller than the uncertainties in the Ar–SF$_6$ potential, especially at the energies associated with the low temperature clusters of interest, so the gain in computational speed is well worth the slight loss of accuracy. Note that since each Monte Carlo step involves the displacement of only a single Ar atom, it is necessary to recalculate only the pair potential values for the atom being moved. However, this potential energy computation consumes the bulk of the computer time required by the simulation, so optimizing this part of the calculation is of considerable practical importance.

Within our model, the force on the Ar atom being moved is simply the sum of the forces exerted by the SF$_6$ molecule and the other Ar atoms in the cluster. The magnitude of the Ar–Ar force is readily obtained by differentiation of Eq. (27). However, an accurate calculation of the force associated with the full Ar–SF$_6$ potential of Pack et al. would be rather complicated because of the complexity of that potential form. Fortunately, the force bias Monte Carlo method requires only a rough estimate of the force felt by the particle being moved. For this part of the calculation, we therefore replaced the full (rigid-body) Ar–SF$_6$ potential by a three parameter function of the form of Eq. (27), which was determined from a least squares fit to the isotropic potential obtained on setting the anisotropy parameters $a_{12}$, $a_6$, and $b_9$ of the Pack et al. potential equal to zero. The resulting effective radial potential parameters $A_{12}$, $A_6$, and $A_9$ are listed in Table III. Note, however, that the full anisotropic rigid-body potential of Ref. 37 was used for the potential energy calculations which determined the accepted cluster structures, and that the simplified function of Eq. (27) was only used in the implementation of the force bias modification of the Monte Carlo procedure.

An event which occasionally occurred in the course of the higher temperature simulations is dissociation of one or more atoms from the cluster. This type of behavior was arbitrarily excluded from the present studies by placing a sphere of radius $12$ Å around the SF$_6$ and rejecting any Monte Carlo move which would have allowed an atom to move beyond this limit. In those cases where dissociation can occur, the resulting simulations should yield the equilibrium average properties for those clusters which remain undisassociated.

III. RESULTS AND DISCUSSION

A. Nature of the synthetic spectra

By analogy with the results of experiments on pure Ar clusters, it is believed that the effective internal temperature associated with the mixed SF$_6$–(Ar)$_n$ clusters studied by Gough et al. lay in the range 30–50 K. The method described above was therefore used to predict the perturbed spectrum of the $v_3$ band of SF$_6$–(Ar)$_n$ for $n$ ranging from 1 to 100, at the two temperatures $T = 30$ and 50 K. The resulting synthetic spectra are presented in Fig. 8, where the frequency is expressed as a displacement from the pure mon-

<table>
<thead>
<tr>
<th>$A_6$ (eV Å$^6$)</th>
<th>$A_9$ (eV Å$^6$)</th>
<th>$A_{12}$ (eV Å$^{12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar–Ar</td>
<td>59.7</td>
<td>-6.95 × 10$^2$</td>
</tr>
<tr>
<td>Ar–SF$_6$</td>
<td>34.6</td>
<td>-6.38 × 10$^4$</td>
</tr>
</tbody>
</table>

omer transition energy of 948 cm\(^{-1}\); the corresponding average frequency shifts are listed in Table IV.

The overall behavior of the simulated spectra is clearly the same at both temperatures. The overriding feature is a monotonically increasing shift to the red as the number of perturbing Ar atoms is increased, combined with a splitting into two peaks for certain cluster sizes. This splitting is particularly prominent for the smallest clusters, appears to be washed out by \(n \approx 9\), reappears with further increases in \(n\) (at least at the lower temperature) and then disappears again for the largest \(n\) values considered.

The systematic growth of the red shift with increasing \(n\) is clearly due to the additive nature of the perturbations, while the splittings are readily understood in terms of structural features of the clusters.\(^{17}\) In particular, for \(n = 1\) the splitting seen in Fig. 8 illustrates the 4:1 ratio of the shifts for the (nondegenerate) parallel and (doubly degenerate) perpendicular components of the \(v_3\) band, as predicted by Eq. (22). As \(n\) increases, the degeneracy of the two perpendicular components is partially lifted, but the magnitude of their displacement from the parallel component of the band remains fairly large until \(n \approx 9\), where it appears to disappear completely. This behavior is readily explained by the continuum model of Fig. 7, if the Ar atoms added as the cluster grows choose to form a close packed unimolecular film wrapping around the SF\(_6\) rather than seek out the pockets of minimum energy in the Ar–SF\(_6\) pair potential (see Fig. 3).

According to the continuum model, addition of Ar atoms is equivalent to lowering the chromophore deeper into the perturbing medium. Figure 7 shows that as the chromophore approaches the perturbing medium from above (positive \(z\) values), the splitting between the parallel and perpendicular bands grows rapidly, passes through a maximum, and then goes to zero when the surface of the chromophore is exactly half covered. As the molecule is lowered further into the medium, the splitting reappears (but with the doubly degenerate perpendicular bands now shifted less than the parallel band), passes through another maximum and finally dies off to zero again as the chromophore sinks deep into the bulk of the perturbing medium. In Ref. 17 it was shown that this same qualitative behavior occurs when a close packed unimolecular film of rigid Ar atoms on the surface of the chromophore is allowed to grow. Thus, the pattern of the splittings seen in the 30 K spectra of Fig. 8 clearly shows that in spite of the strong asymmetry of the Ar–SF\(_6\) pair potential, the Ar atoms preferentially form a close-packed unimolecular layer wrapped around the SF\(_6\). In accord with the structural studies of Ref. 17, this also indicates that 8–9 Ar atoms suffice to form a hemispherical “cap” which approximately half covers the SF\(_6\), while ~17 atoms are required to form a closed shell.

The same trends discussed above are also seen in the higher temperature (50 K) results, although the structure is more washed out by the thermal averaging. In particular, the band splitting associated with more-than-half complete cov-
verage becomes an ambiguous broadening, while the high-"n" spectral narrowing does not occur until very large "n" values are reached. However, for n \geq 15 the 50 K synthetic spectra no longer seem to change in a completely systematic way with further increases in "n". This latter behavior is attributed to a lack of convergence of those simulations.

For the smaller clusters, a force bias Monte Carlo calculation based on $1 \times 10^6$ accepted moves yields reproducible spectra with smaller statistical uncertainties. However, the quality of the statistics decreases systematically with increasing "n", and for n \geq 15 it became clear that runs of only $1 \times 10^6$ accepted moves do not readily yield convergence to the desired canonical distribution of cluster structures. In other words, after only $1 \times 10^6$ steps, results obtained from runs which used different types of initial configurations now showed some dependence on the starting conditions. This was particularly noticeable at the lower temperature, where the larger clusters displayed a penchant for locking themselves into various metastable configurations. For this reason, no 30 K results are reported for n > 18. At the higher temperature, although a wide variety of cluster structures are accessed in a given run, the loss of systematic trends in the spectral shapes for n > 15 provides convincing evidence of this lack of convergence.

In spite of the above, it appears that the average shifts are less sensitive to the details of the cluster structure than they are to the overall density of packing the Ar atoms around the SF$_6$ molecule, so the average spectral shifts yielded by our simulations are still believed to be meaningful (albeit somewhat uncertain) for n > 15 clusters, even at 50 K. However, the peak widths and shapes in this region should only be taken to be qualitatively correct, especially at the higher temperature. Table IV shows that for cluster sizes up to n = 18, the average shifts are distinctly smaller at 50 than at 30 K. This will be interpreted as evidence for cluster isomerizations in which the unimolecular film of Ar atoms switches over to a double- or multilayer structure, since atoms in an outer layer would contribute relatively less to the spectral shift. Moreover, at this higher temperature there is a greatly enhanced probability of cluster dissociation.

B. Comparisons with experiment and cluster size distribution effects

The experimental spectra of Ref. 14 are shown in Fig. 9, and the behavior of their peak shifts and widths is summarized in Fig. 10.$^{52}$ In the experiments, larger average cluster sizes were produced by increasing the backing pressure of the nozzle expansion. However, except for the lowest pressure expansions, which are expected to yield mainly dimers, a distribution of cluster sizes is produced under most experimental conditions, so it is difficult to associate the observed spectra with particular values of n. In spite of this problem, comparisons with the source conditions associated with the results of Farges et al.$^{51}$ yielded the approximate cluster size scale shown on the top of Fig. 10.

Aside from the peak splitting in the simulated spectra for very small n, the simulated and experimental spectra and their dependence on cluster size are clearly qualitatively the same. For the smaller clusters, the spectrum is relatively narrow and only slightly displaced from the free SF$_6$ transition frequency, while the peak shifts monotonically to the red with increasing n, and in the high pressure or high-n limit, approaches the frequency associated with the known matrix spectrum (uppermost segment of Fig. 9).$^{53,54}$ The absence of bimodal behavior in the lowest pressure experimental spectra$^{14,52}$ may be partly due to cluster size averaging. However,
it most likely demonstrates that these smaller clusters are relatively hot, since Fig. 8 shows that thermal averaging can wash out even the marked 4:1 shift ratio which occurs for fixed configuration \( n = 1 \) clusters.

In contrast to the above, the fact that bimodal behavior analogous to that seen in the 30 K simulations for \( n = 11 \) to 14 is not resolved experimentally is almost certainly due to cluster size averaging effects. Molecular dynamics simulations have now shown that at temperatures above 40 K these larger clusters dissociate on a nanosecond time scale. On the other hand, time of flight arguments show that the lifetimes of the clusters observed in the experiment must be of the order of milliseconds. Thus, the larger observed clusters must be relatively cold, so thermal averaging alone would not explain this loss of structure. However, from consideration of Fig. 8, it is readily apparent that averaging over even a relatively narrow distribution of cluster sizes would wash out the details of this bimodal structure and yield a single, relatively broad spectral peak.

With or without averaging over cluster size distributions, the simulations predict a local maximum in the overall width of the spectrum for (average) cluster sizes in the neighborhood of \( n = 13 \). This is illustrated by the solid curves in Fig. 11 which plot the full widths at half-maximum vs average cluster size for synthetic spectra generated for a single cluster size at a time (\( \sigma_n = 0 \)), as well as for those obtained on averaging over a Gaussian distribution of cluster sizes characterized by the parameter \( \sigma_n \) (see below). This behavior seems to correlate well with the observation of a maximum in the widths of the experimental spectra for pressures in the neighborhood of 4300 Torr (see Fig. 10). This agreement appears to suggest that the observed broadening provides experimental confirmation that an incomplete layer of Ar atoms will preferentially form a close-packed “cap” on one side of the SF\(_n\) rather than first fill the minimum energy pockets at the octahedral sites of the pair potential (see Fig. 3). However, the alternate explanation described below must also be considered.

At the time the experiments were done, this broadening was attributed solely to the differences among the frequency shifts for the various cluster sizes present in the beam. While the nature of the cluster size distributions produced in such expansions is still poorly understood, we attempted to estimate their effect on the simulated spectra by averaging over the “single-\( n \)” spectra of Fig. 8 while assuming a simple Gaussian distribution of cluster sizes. To this end, averaged spectra for \( T = 50 \) K were generated from the expression

\[
\tilde{f}_n(\nu) = \sum_n f_n(\nu) e^{-\left(\nu - \nu_0(n')/2\sigma_n^2\right)^2/\sum_n e^{-\left(\nu - \nu_0(n')/2\sigma_n^2\right)^2/2\sigma_n^2},}
\]

(28)

where \( f_n(\nu) \) is the spectral line shape obtained for the single cluster size \( n' \), and \( \tilde{f}_n(\nu) \) the line shape resulting from this convolution. As the size distribution is expected to become broader with increases in the average cluster size \( n \), the parameter \( \sigma_n \) characterizing the width of the distribution function was assumed to be proportional to \( n \). The solid points joined by solid lines in Fig. 11 show the dependence on \( n \) and \( \sigma_n = k \times n \) of the full widths at half-maximum (FWHM) of the peaks in the convoluted spectra \( \tilde{f}_n(\nu) \) generated on substituting the actual synthetic line shapes of Fig. 8 into Eq. (28), for \( k = 0.0, 0.1, 0.25, \) and 0.5. As \( \sigma_n \) increases, the magnitudes of the simulated widths also increase, and the linewidth curves become increasingly similar to the plot of the experimental linewidths seen in the upper half of Fig. 10.

Since the red shifts of the peaks in the simulated spectra are not a linear function of the cluster size parameter \( n \) (or \( n' \)), the convolution of Eq. (28) would cause a broadening of the \( f_n(\nu) \) peak for average cluster sizes near the steepest portion of the peak shift vs \( n \) curve, even if the linewidths of the single-\( n' \) \( f_n(\nu) \) spectra were independent of \( n' \). This was the mechanism suggested by Gough et al. as the source of the linewidth maximum seen in Fig. 10. As a quantitative test of this suggestion, we repeated the convolutions described above, except with the actual single-\( n' \) synthetic spectra of Fig. 8 replaced by a simple Gaussian line shape whose peak shifted with \( n' \) in the appropriate manner, but whose widths were independent of \( n' \):

\[
f_n(\nu) = e^{-\left(\nu - \nu_0(n')/2\Gamma^2\right)^2},
\]

(29)

where \( \nu_0(n') \) is the red shifted average frequency listed in Table IV, and the width parameter \( \Gamma \) was fixed at the value 0.5 cm\(^{-1}\) chosen to make the convoluted linewidths agree with experiment for small \( n \). For the same four \( \sigma_n \) values
considered above, the linewidths of the resulting convoluted spectra are shown as open points joined by dashed lines in Fig. 11. These plots represent the broadening due to the frequency shift and (assumed) cluster size distribution alone, without taking the line broadening of the single-\( n \) spectra into account.

The results of Fig. 11 show that for narrow cluster size distributions (i.e., small values of \( \sigma_c \)), the width of an observed spectral line can be associated with the inherent properties of the single-cluster-size spectra. In this case, the behavior of such bandwidths would provide evidence for the structural proclivities of the clusters. However, as the cluster size distribution becomes broader, it eventually becomes impossible to distinguish the effects of size distribution and band shifts from those of inherent line broadening. Even without a detailed knowledge of the cluster size distribution, it may sometimes be possible to empirically distinguish between these two situations by a careful examination of the details of the line shape or of the linewidth vs average cluster size curve. This is impossible with the data of Ref. 14 because of its low resolution, but this situation may improve when the results of better experiments\(^5\) become available.

In conclusion therefore, the agreement between the experimental and simulated spectra must be considered at least semiquantitative. The nature of the frequency shift curves are quite similar (see Fig. 1 of Ref. 16) and the 7 cm\(^{-1}\) shift of the synthetic spectra for the largest cluster sizes considered is fairly close to the 9 cm\(^{-1}\) observed experimentally. Indeed, in view of our neglect of all but the induced-dipole contribution to the spectral shift and the possible effects of inaccuracies in the Ar-SF\(_6\) pair potential, this agreement is really excellent. In addition, while the experimental peak widths are distinctly larger than those of the synthetic spectra of Fig. 8, this apparent disagreement is largely removed if one makes allowances for a polydisperse cluster size distribution. Of course, in view of the unknown size distribution in the experiment and the fact that the cluster size scale in Fig. 10 is only approximate,\(^1\) the agreement thus obtained has only qualitative significance. However, the overall agreement attained seems to provide good confirmation of the validity of the model underlying the present work.

C. Cluster Isomerization

In the discussion of Table IV, it was pointed out above that the smaller shifts predicted for the higher temperature could be interpreted as evidence for an increasing degree of isomerization from structures in which the Ar atoms form a close-packed single layer wrapping around the SF\(_6\) to multilayer structures characterized by distinctly larger average Ar-SF\(_6\) distances. In examining this question further, we looked for correlations between the frequency shifts and features of the cluster structure during the Monte Carlo "walk" through configuration space. To this end, the properties of 12- and 16-Ar atom clusters at \( T = 50 \) K were examined after each 5000 (of 1 \( \times 10^6 \)) accepted Monte Carlo moves. For the resulting 200 sample configurations, Figs. 12 and 13 show the evolution of both (lower segments) the average frequency shift for the three \( \nu_3 \) components, and (upper segments) the magnitude of the displacement of the center of mass of the \( n \) Ar atoms from the center of the SF\(_6\) molecule.

The most prominent feature of Figs. 12 and 13 is simply the very strong correlation between the changes in the frequency shifts and those in the displacements of the (Ar)\(_n\) center of mass from the center of the SF\(_6\). Larger red shifts are typically associated with clusters in which the (Ar)\(_n\) center of mass is fairly close to the center of the SF\(_6\), while the smaller shifts correspond to structures in which this displacement is relatively large. In other words, large shifts occur when a unimolecular layer of Ar atoms is wrapped around the SF\(_6\) chromophore, while the smaller shifts are associated with multilayer "solvent" structures in which the SF\(_6\) effectively lies on the surface of the cluster, displaced some 3-4 Å from the (Ar)\(_n\) center of mass. Note that the smaller minimum values of the (Ar)\(_n\) displacements for the \( n = 16 \) case merely reflects the fact that 16 Ar atoms form a nearly closed shell around the SF\(_6\) molecule, while 12 do not.

In the course of the Monte Carlo walk, it appears that the system typically retains one or the other of these two types of structures for a considerable number of steps, and hops back and forth between them with only a small fraction

\[ \text{FIG. 12. Values of (upper half) the distance from the (Ar)\(_n\) center of mass to the S atom, and of (lower half) the average SF\(_6\) frequency shift, as evaluated for every 5000th accepted configuration of a force bias Monte Carlo simulation for SF\(_6\)-(Ar)\(_n\) at } T = 50 \text{ K.} \]

\[ \text{FIG. 13. As in Fig. 12, for SF\(_6\)-(Ar)\(_n\) at } T = 50 \text{ K. The 250 000 configurations associated with the two intervals A and B are analyzed further in Fig. 14.} \]
of the configurations being associated with intermediate structures. For \( n = 12 \) (see Fig. 12) the system is found most often with structures for which this displacement is large and the red shift is small, while for \( n = 16 \) (Fig. 13) the phase with the larger red shifts and smaller displacements is preferred at this temperature. Furthermore, the hopping between the two structures occurs more frequently for the smaller cluster, which suggests that the mobility of the Ar atoms in the \( n = 12 \) cluster is higher than that for \( n = 16 \).

The behavior described above is strikingly similar to the kind of hopping between classes of liquid and solid-like structures seen in the molecular dynamics simulations of pure Ar clusters reported by Jellinek et al.\(^6\) In that study it was demonstrated that these two "phases" coexist in a stable equilibrium over a finite range of temperatures close to the region of interest here, and that the clusters spontaneously "switch" back and forth between the two phases, with the time spent in each form being very long relative to the time required to establish the properties characteristic of the new phase. Although our results cannot be directly compared with theirs because of the different potential energy functions used, it is tempting to associate the two classes of structures identified here with their two phases.

In an effort to further clarify this question, we examined the properties of the two sequences of 250 000 configurations associated with the intervals labeled A and B in Fig. 13. In A, the cluster structures are largely of the single-perturber-layer type which yields relatively larger frequency shifts, while in B the multilayered perturber structures which give rise to smaller red shifts predominate. For these two cases, the Ar–S and Ar–Ar radial distribution functions, the average potential energy per Ar atom, and the simulated absorption spectrum are shown in Fig. 14. While the main peak near \( r_{\text{Ar-S}} = 4.5 \) Å appears in the Ar–S radial distribution functions for both classes of structures, a noticeable second peak near \( r_{\text{Ar-S}} = 7 \) Å occurs only for the smaller-frequency-shift case B clusters. This confirms the conclusion that the latter are indeed structures in which the Ar atoms are piled up together on one side of the SF\(_6\), while the larger-frequency-shift class A clusters correspond to a single close-packed layer of Ar atoms wrapped around the SF\(_6\).

For both cases A and B, the Ar–Ar radial distribution functions in the second segment of Fig. 14 have three distinct maxima lying approximately at \( r_{\text{Ar-Ar}} = 3.75, 7.0, \) and \( 8.5 \) Å. However, in the configurations associated with the smaller-frequency-shift interval B, the two outer peaks are more smeared out than in case A, which suggests that the latter corresponds to a more ordered or rigid type of structure. These observations support the suggestion that these two classes of structures correspond to solid- and liquid-like phases. It is interesting to note, however, that the distributions for the average potential energy per Ar atom seen in Fig. 14 are fairly similar for these two cases. Since the potential energy difference between these two classes of structures is fairly small, the predominance of one over the other may be mainly determined by entropy considerations.

Another perspective on this apparent isomerization equilibrium is provided by an examination of the temperature dependence of the spectra and properties of SF\(_6\)-Ar clusters. These results are shown in Fig. 15 where the same four distributions examined in Fig. 14 are plotted for temperatures varying from 20 to 70 K. In the simulated spectra, shown on the extreme right, the broad peak observed at around \( T = 55 \) K becomes narrower and shifts farther to the red as the temperature is decreased, while it also becomes narrower, but shifts back towards the free SF\(_6\) transition frequency as the temperature is raised. At the same time, the features of the radial distribution functions associated with more ordered behavior are lost as the temperature is increased. It is conventional to associate such changes with a solid–liquid phase change when they occur as functions of temperature. However, the same types of characteristic differences in these distributions appeared in Fig. 14 for different intervals of a single simulation at a single temperature. Thus, the results seen in Figs. 13–15 seem in accord with the idea that the surrounded-chromophore larger-frequency-shift structures are solid-like while the surface-chromophore smaller-shift structures are liquid-like.

In concluding this discussion, it is important to remember that while the arguments presented above are fairly persuasive, they are indirect. In particular, while it is tempting to think of the Monte Carlo walks of Figs. 12 and 13 as representing the time evolution of these systems, it is simply not correct to do so. Thus, firm conclusions regarding the longevity and relative rigidity of the different types of struc-
tures, and of the possibility of using their infrared spectra to monitor the behavior of these mixed clusters, must await molecular dynamics studies which will introduce a real time scale. Such a study is now under way in this laboratory.55

IV. CONCLUDING REMARKS

The good qualitative agreement between experiment and theory seen on comparing Fig. 8 with Fig. 9, and Fig. 11 with the upper segment of Fig. 10, demonstrates the validity of the model and of the computational approach used in the present work. The combination of the instantaneous dipole–induced dipole mechanism with a force bias Monte Carlo averaging procedure clearly yields a description of the infrared spectrum of an SF₆ molecule in an (Ar)_ₙ cluster which is in near-quantitative agreement with experiment. This in turn gives us confidence that other implications of these simulations are physically significant.

It is important to remember, however, that the quality of these results rests on two foundations. The first is simply the fact that both the Ar–Ar and the Ar–SF₆ interaction potentials are reasonably well known.37,38 This allows the Monte Carlo averaging procedure to provide a realistic estimate of the true canonical distribution of cluster configurations for these systems. For most other infrared active molecules in cluster or matrix surroundings, analogous high quality intermolecular potential information is unfortunately not yet available. For example, although similar photodissociation experiments have been performed for Ar clusters seeded with CH₃F or SiF₄ chromophores in place of the SF₆,14,52,58,59 the absence of reliable interaction potentials for these systems would make analogous simulations much more speculative.

The second major assumption of the present treatment is that the instantaneous dipole–induced dipole model provides the dominant contribution to the frequency shifts. This should be a realistic approximation as long as the transition dipole moment in question is fairly strong, and should apply to a wide variety of systems, independent of whether or not the chromophore has a permanent dipole moment. Such a permanent dipole would not vitiate the present mechanism because the frequency shifts are caused by the change in the intermolecular interaction associated with the variation of the instantaneous dipole during the intramolecular vibration, coupled with the fact that the amplitude of this intramolecular motion (and hence the strength of the interaction) increases with vibrational excitation.

Improvements to the computational scheme used in this paper can be made by including the influence of the short-range overlap repulsion and the attractive dispersion terms on the stretching dependence of the atom–molecule interaction potential. As was demonstrated in Sec. II B, the present pairwise additive functions may adequately serve this purpose, but more sophisticated forms should also be considered. The instantaneous dipole–induced dipole model for the frequency shifts could also be improved. In particular, the dependence of the transition intensities on cluster structure could be taken into account, while the effect of screening of the electric field of the molecule by the atoms closest to it, and many-body terms such as the triple–dipole interaction, should also be examined. In addition, the implications of the fact that the vibrationally distorted chromophore is not a point dipole, and of the distributed nature of the atomic polarization deserve further study. However, although such improvements would change the details of the results, the essential conclusions of the present paper would not likely be affected.

In view of both the remaining uncertainties in the Ar–SF₆ potential energy surface and its stretching dependence, and other approximations introduced to facilitate the present simulations, it is not surprising that in detailed comparisons with experiment, some discrepancies remain. For example, the limiting frequency shift observed for very large SF₆₋(Ar)_ₙ clusters is ~9 cm⁻¹, while our simulation gives only ~7 cm⁻¹ for SF₆₋(Ar)₁₀₀ at 50 K, and a continuum estimate of the influence of Ar atoms lying farther from the SF₆ suggests that our calculated shift for n = 100 is within 0.2–0.3 cm⁻¹ of the fully converged value for an infinitely large (model) system. At the same time, a comparison between the experimental and theoretical linewidths can be only qualitative because of the uncertainties regarding both the experimental cluster size distributions and the effective temperature of the clusters. It is also not clear whether a description based on the idea of a canonical distribution with a well defined temperature is an appropriate basis for such comparisons.

In conclusion, therefore, a computational scheme has been developed which provides a realistic description of the shifting and broadening of the ν₃ band of SF₆ in SF₆₋(Ar)_ₙ clusters. Its use has led to predictions regarding the existence and spectral properties of two distinct classes of cluster structures and intriguing suggestions regarding their dynamical behavior. However, because of uncertainties regarding the experimental cluster temperature and cluster size distribution, it is not yet possible to relate such predictions to experimental observables. Moreover, the question of whether the two classes of structures correspond to the solid- and liquid-like phases found to coexist for pure Ar clusters under similar conditions,50 cannot yet be answered, although molecular dynamics calculations to resolve this question are currently under way.55

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Better resolved experimental spectra taken over a wider range of conditions have now been obtained by X. Gu, B. Zhuang, N. Isenor, and G. Scoles (private communication, 1987).
Note that the apparent structure near \( n = 15 \) in the plot for \( \sigma_n = 0 \) is probably an artifact of incomplete convergence of the simulations in this region.
Note that it is this line broadening in the simulated spectra for cluster sizes \( n = 13-18 \), later reassigned (Ref. 17) as due to the structure based splitting effects illustrated by Fig. 7, which was incorrectly identified in Ref. 16 as a possible observable manifestation of phase coexistence.